# The Influence of Major Ion Chemistry on the Transport of Uranium from a Restored ISR Zone Following In-Situ Mining

## Abstract

## Introduction

Powertech Uranium Corporation (Powertech) has proposed using in-situ recovery methods to mine uranium at the Dewey Burdock site in the southwestern region of the Black Hills of South Dakota (fig. 1). The uranium recovery license application by Powertech to the United States

*Figure 1. Location of the Dewey Burdock Site in South Dakota*

Nuclear Regulatory Commission (NRC) is publicly available and contains background information about the site along with technical details and baseline sampling data (http://www.nrc.gov/materials/uraniumrecovery/license-apps/dewey-burdock.html - with detailed application documents under the "application documents" link). A brief summary of the site history is provided by Powertech at http://www.powertechuranium.com/s/DeweyBurdock.asp.

At the Dewey Burdock site, uranium occurs as roll-front ore bodies in several sandstone units of the Inyan Kara Group of Early Cretaceous Age (Johnson et al, 2013). Uranium roll-front ore bodies develop as groundwater leaches uranium from a source rock, for example, a volcanic ash fall deposit, and transports the dissolved uranium through porous and permeable sandstone or conglomerate (Figure 2). When the dissolved uranium encounters a reducing environment uranium precipitates out of solution as a solid phase such as the mineral uraninite ($UO_2$).

[ PAGE \* MERGEFORMAT ]

*Figure 2. Conceptual Model of a Uranium Roll Front Deposit*

The relatively low-grade U in these deposits and their location in young, near-surface, permeable sandstones make in situ recovery (ISR) feasible. Uranium ISR reverses the process that caused them to be deposited. The process involves the addition of oxygen and complexing agents such as carbon dioxide or sodium bicarbonate to form a lixiviant, which is circulated through a well field developed around the rolls, oxidizing the U from U(IV) to U(VI) and dissolving it (Fig. 3). The groundwater containing aqueous U (pregnant lixiviant) is pumped to

*Figure 3. Diagram of a generic uranium ISR process*

the surface, and the U is removed from solution in ion exchange tanks. The "barren" lixiviant is then re-fortified with oxygen and a complexing agent and recirculated through the ISR well field (Fig. 1). Slightly more water is extracted than injected in order to maintain an inward hydraulic gradient to prevent the movement of the lixiviant into portions of the aquifer not targeted for U recovery. Once U recovery is complete, well fields are generally restored by flushing the recovery zones using either local or treated groundwater. The U ISR zones are then referred to as "restored zones".

At the Dewey Burdock site all proposed well fields in the Dewey portion and several of the proposed well fields in the Burdock portion have reduced groundwater downgradient of the ISR areas. Three of the well fields in the Burdock portion of the site have oxidizing groundwater downgradient of the ISR zone (Figure 4). In general, U is expected to be less mobile in reducing

*Figure 4. Location of the wells fields at the Dewey Burdick site showing the location of downgradient reduced and oxidized zones*

zones due to the greater potential for U precipitation and sorption than in the oxidized zone based on the mineralogy, as this is the controlling mechanism for the original formation of the U deposit. This potential for higher U mobility in the oxidized zone is the reason for focusing on this area with reactive transport modeling, as the oxidized zone poses a greater concern for

meeting regulatory compliance (no change in groundwater quality at the aquifer exemption boundary).

Preliminary 1-D reactive transport modeling using the USGS geochemical code PHREEQC (Parkhurst and Appelo, 2013) by the United States Environmental Protection Agency (EPA) Region 8 Office in Denver, Colorado as part of the permit review process has indicated that the major ion chemistry in the restored ISR zone can potentially have a major influence on uranium attenuation in the oxidized downgradient zones. This paper presents the results of 1-D reactive transport modeling of uranium downgradient from a restored ISR zone using groundwater of two different major-ion water types in the restored ISR zone and the processes responsible for the different results.

## Reactive Transport Modeling

The one-dimensional reactive transport modeling capability of the USGS geochemical code PHREEQC (Parkhurst and Appelo 2013) using the minteq.v4.dat database was used to simulate the transport of uranium from the Restored ISR zone to the aquifer exemption boundary. The one-dimensional transport model domain was the same as shown in Figure 4 in Johnson and Tutu (2015) (Figure 5). There are 60 cells in the model and each cell was 5 meters in length

*Figure 5. One-Dimensional Reactive Transport Model Domain*

based on a groundwater flow velocity of 5 m/yr reported by Johnson and Tutu (2015). Cells 1-20 represent the Restored ISR zone (100 m) and cells 21-60 represent the downgradient oxidized zone (200). The aquifer exemption boundary is at cell 40, 100 meters downgradient from the end of the Restored ISR zone. Each year there is a cell-to-cell shift and as groundwater in each cell moves to the next cell, the water interacts with the solid phase specified in the next cell. To simulate these reactions, the PHREEQC database was modified to include the

[ PAGE \* MERGEFORMAT ]

calcium/magnesium uranyl carbonate complexes reported by Dong and Brooks (2006) and recently updated U thermodynamics (Guillaumont et al. 2003)". The uranium complexes that were included in the modeling are: $Ca_2UO_2(CO_3)_3$, $CaUO_2(CO_3)_3^{-2}$, $MgUO_2(CO_3)_3^{-2}$, $UO_2(CO_3)_3^{-4}$, $UO_2(CO_3)_2^{-2}$, and $UO_2^{+2}$.

Adsorption of uranium can occur on the surface of oxyhydroxides or hydrous ferric oxides (ferrihydrite – $Fe(OH)_3$), clays, and organic matter. The $UO_2^{+2}$ ion is the only uranium species that will significantly adsorb to these surfaces (references). In PHREEQC there are two options to model uranium adsorption. One option is to model adsorption onto oxyhydroxides or hydrous ferric oxides (HFO in PHREEQC). This requires data on the mass of ferric hydroxides in the aquifer. A second option and the one used by Johnson and Tutu (2015) is to use the generalized composite surface complexation models which allows for the modeling of adsorption onto any surface capable of interacting with uranium not only oxyhydroxides or hydrous ferric oxides but also clays and organic matter. So, the surface complexation model accounts for total adsorption without having to calculate or estimate adsorption parameters for each mineral. The equilibrium constants and site densities for the adsorption surfaces are obtained by performing the batch tests described in Johnson and Tutu (2015).

Water quality data for the wells used in the modeling scenarios are presented in table 1. Two scenarios were modeled that differed in the groundwater in the restored ISR zone. In one scenario well 684 groundwater was in the restored ISR zone (cells 1-20) and in the second scenario Madison Limestone groundwater was in the restored ISR zone with both groundwaters assigned a uranium concentration of 200 µg/L. In both scenarios groundwater from well 684 was used in the area downgradient of the restored ISR zone as was done in Johnson and Tutu (2015). Based on the position of wells in the area of well 684 as depicted on Figure 2 in Johnson (2012)

well 682 was considered upgradient of well 684 and was selected as representative of incoming background groundwater into the model domain for both scenarios (Solution 0 in PHREEQC).

## Uranium at the Aquifer Exemption Boundary with Well 684 Groundwater in the Restored ISR Zone

The concentration of uranium at the aquifer exemption boundary over 300 years when well 684 groundwater is in the restored ISR zone is shown in figure 6. Diffusion and diffusivity were not included in these models since only chemistry is being evaluated. Uranium concentration that changes as a result of advection only (chemical changes and adsorption not included) show that up to year 19 the uranium concentration is 24.1 µg/L and is the uranium in well 684 groundwater. At year 20 groundwater from well 684 with a uranium concentration of 200 µg/L reaches the aquifer exemption boundary and takes 20 years to traverse it. At year 40 groundwater
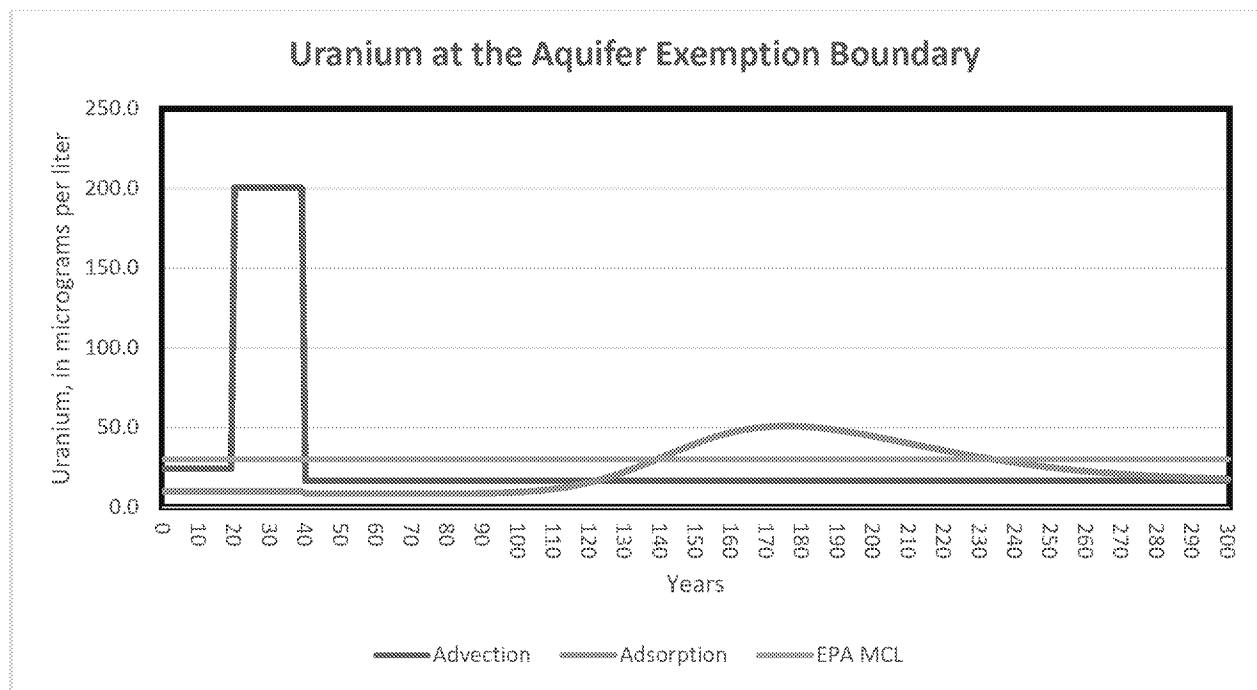


Figure 6. Uranium at the aquifer exemption boundary when well 684 groundwater is in the restored ISR zone

from upgradient well 682 with a uranium concentration of 16.4 μg/L reaches the aquifer

exemption boundary and the uranium concentration remains at 16.4 μg/L until year 300.

The difference in the concentration of uranium between the advection and adsorption curves

represents the mass of uranium removed from solution as a result of adsorption. Through year 39

the concentration of uranium in groundwater is consistently 9.9 μg/L and decreases slightly to

8.4 μg/L from year 40 to year 83. Uranium concentrations then start to increase at year 84 and

exceed the EPA MCL of 30 μg/L from years 143 to 227.

## Uranium at the Aquifer Exemption Boundary with Madison Limestone Groundwater in the Restored ISR Zone

The concentration of uranium at the aquifer exemption boundary over 300 years when well

Madison Limestone groundwater is in the restored ISR zone is shown in figure 7. A major

difference in the concentration of uranium over time in this scenario compared to when well 684
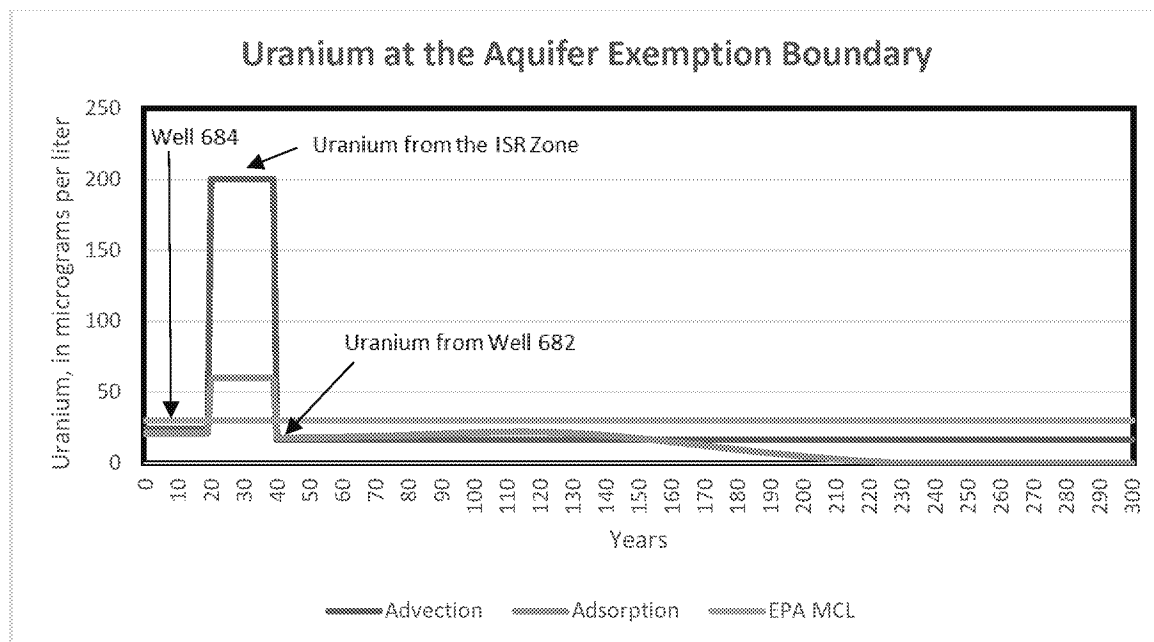


Figure 7. Uranium at the aquifer exemption boundary when Madison Limestone groundwater is in the restored ISR zone

groundwater was in the restored ISR zone is that the concentration of uranium never exceeds the

EPA MCL.